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DIPHENYLBORIC ACID AND ITS DERIVATIVES

By

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The first mention of diphenylboric acid was made in 1894 by Michaelis, who attempted to prepare it by saponification of diphenylboron chloride. He described diphenylboric acid as a crystalline substance with a melting point at 264-267°C¹. Later Michaelis thought he obtained diphenylboric acid as a product of hydrolysis of diphenylboron bromide, boiling at 215-235°C at 15 mm, and which solidified in the receiver². According to the data of Smig, diphenylboric acid was obtained by the action of excess of phenyl magnesium bromide on tri-iso-butyl borate. He described diphenylboric acid as a substance with a boiling point of 150-155°C, at 20 mm and melting point of 37.5°C³.

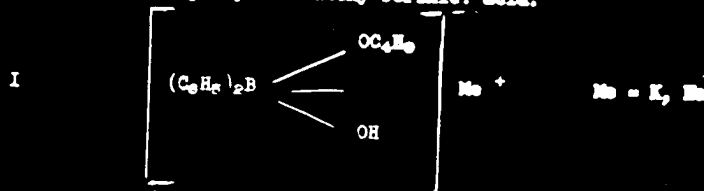
During the investigation of the action of arylmagnesium bromides on boric acid esters, the authors have established this reaction as a convenient method of synthesis of esters of diarylboric acids.

Thus isobutyl ester of diphenylboric acid was obtained in 57% yield by the action of 2 moles of phenylmagnesium bromide on 1 mole of triisobutylborate in the 70-75°C temperature range.



The isobutyl ester of diphenylboric acid, in contrast with di-isobutyl ester of phenylboric acid, is extremely stable with respect to hydrolytic action of not only water but also dilute mineral acid (hydrochloric acid) hydrolysis of isobutyl ester of diphenylboric acid at 60-70°C for a period of 1-2 hours in alcoholic or water media. Upon raising the temperature and increasing the time of the reaction, phenylboric acid is obtained as product. Isobutyl ester of diphenylboric acid is not saponified by the action of dilute water solutions of alkali hydroxides, but unexpectedly it is surprisingly soluble in them.

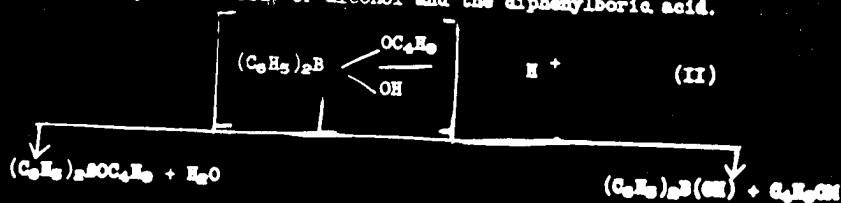
A more detailed study disclosed complex formation resulting during dissolution of isobutylester of diphenylboric acid in alkali hydroxides. These complexes (I) are salts of diphenyl isobutoxy borinic acid.



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Borinic acids are complex acid of quadrivalent negative boron, inverse to the ammonium ion type in which the central atom is negatively charged, analogous to the carbonate ion. The substituted borinic acids are derived from the hypothetical $B(OH)_4H$.

Acidifying the alkali salt (I), the acid (II) is obtained. This acid is unstable; it decomposes in two directions either yielding water and the original ester of diphenylboric acid, or alcohol and the diphenylboric acid.

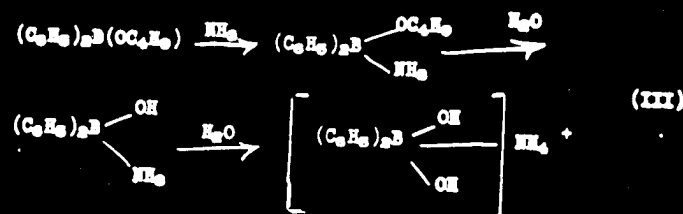


The original ester, $(C_6H_5)_2B(OC_4H_9)$, is obtained back in 36% yield, while the diphenylboric acid is obtained as its anhydride in 17% yield.

Stability of esters of diphenylboric acid with respect to hydrolytic agents can be explained by the greater tendency of the complex borinic acid (II) to split out water than alcohol.

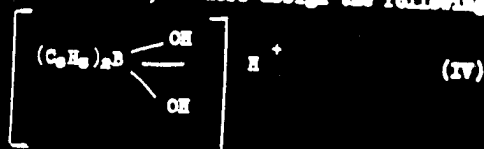
The mechanism of saponification, described above, through a complex formation, is quite general for esters of diphenylboric acids.

Reaction between an ester of diphenylboric acid and aqueous ammonia leads to formation of insoluble ammonium salt (III) according to the following scheme:



This scheme, presupposing formation of a rather reactive ester of diphenylboric acid with ammonium hydroxide, accounts for the relative ease of saponification of diphenylboric acid esters with aqueous ammonia.

Acidification of the water suspension of ammonium salt (III) yields a liquid substance with melting point at -35 $-35^\circ C$, analysis of which shows it to be monohydrate of diphenyl boric acid; authors assign the following structure to it:



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Acid (IV) is very unstable and in vacuum or upon slight heating changes to the anhydride of diphenylboric acid (V) obtained by HCl from sodium tetraphenylboron.



Diphenylboric acid anhydride upon action of potassium hydroxide or ammonium hydroxide does not yield salts of diphenylboric acid, but salts of acid (IV).

Properties of diphenylboric acid and its derivatives clearly show that it was not the acid obtained by previous investigators.

EXPERIMENTAL

Isobutyl ester of Diphenylboric Acid.

One half mole (58 grams) of triisobutyl borate in 200 ml of anhydrous ether were added to one mole of phenylmagnesium bromide in 500 ml of anhydrous ether within a period of one hour with rapid agitation at -90 to -60°C . Upon addition of all the borate, agitation of reaction mixture was continued for 6-7 hours at -70 to -75°C . On the next day, the reaction mixture was treated with 600 ml of water acidified with 100 ml of concentrated hydrochloric acid. The ether layer was then separated and the water layer shaken several times with fresh portions of anhydrous ether. The ether extracts were then combined and the ether distilled off at atmospheric pressure. Isobutyl alcohol was next removed under vacuum of water aspirator. The remaining liquid was then fractionated under atmosphere of nitrogen using a Buepel column. About 60-65 grams of product were collected at $136-135.5^\circ\text{C}$ (3 mm Hg) representing 51-57% of theoretical yield. The product was redistilled at 2.5 mm Hg and $129.5-130^\circ\text{C}$. The residue was found to be phenylboric acid anhydride. It was washed with isopentane and dried in the air. Yield of anhydride was 7-11 grams, melting point $190-192^\circ\text{C}$ (block, sealed capillary), 18-19% theory.

Analysis of sample showed it to contain 80.86% C, 7.97% H, theoretical for $\text{C}_{12}\text{H}_{12}\text{BO}$ - 80.69% C, 8.04% H.

Determination of boron and of phenyl groups was done by the method of Wittig⁴.

Found % C_6H_5 64.71 % 4.40

Theory ($\text{C}_{12}\text{H}_{12}\text{BO}$)% C_6H_5 64.79 % 4.54

Diphenylisobutylborosodium (I).

2.3424 grams (0.00984 moles) of isobutyl ester of diphenylboric acid were dissolved in 9.85 ml of 1N sodium hydroxide. The solution was concentrated by

evaporation almost to dryness in the vacuum dessicator. The crystals were then recrystallized from a mixture of benzene and alcohol (20:1). The crystals were then sucked dry washed with benzene and dried under vacuum. 1.5 grams of colorless, crystalline product were obtained. The product is soluble in water, methanol and ethanol and insoluble in hexane, benzene and chloroform. The water solution can be titrated with acid just like free sodium hydroxide.

Found % $C_{12}H_{10}$ 56.25; %N 4.01; %Na 8.99

Theory ($C_{12}H_{10}O_2Na$) % $C_{12}H_{10}$ 55.43; %N 3.89; %Na 8.86

Decomposition of Diphenylisobutoxyboranesodium in Acid Media.

10 grams of isobutylester of diphenylboric acid are dissolved in 20 ml of 10 percent sodium hydroxide.

The resulting solution is acidified with 5 ml of concentrated hydrochloric acid. The oil that is separated is extracted with ether. The ether is then removed in vacuum, the residue is heated for 5 minutes on a steam bath, after which the ester of diphenylboric acid is distilled in a stream of nitrogen. 3.3 grams of isobutyl ester of diphenylboric acid are obtained (m.p. 130-132°C/4 mm).

As a result of recrystallization from benzene of the residue from above distillation, 1.25 grams of colorless, crystalline substances were obtained with a melting point 130-132°C. Mixed melting point determination using the above crystalline material with diphenylboric acid anhydride also melted at 130-132°C.

In this manner, as a result of acid decomposition of diphenylisobutoxyboranesodium, a 55 percent yield of isobutylester of diphenylboric acid and a 17 percent yield of diphenylboric acid anhydride were obtained.

Diphenyldiisobutoxyboranesodium (III).

Seven ml. of twenty percent aqueous ammonia are added to 2.1 grams of isobutylester of diphenyl boric acid. The resulting precipitate, appearing after a few minutes, is sucked dry and then dried in air, after which it is recrystallized from benzene. 1.65 grams of colorless, crystalline product are obtained (m.p. at 109-110°C (with decomposition)). Yield represents 67% of theory. For determination of nitrogen, a known weight of product is boiled with excess 0.2N sodium hydroxide.

The excess alkali is then titrated with .1N acid

Found % $C_{12}H_{10}$ 71.29; %N 5.36; %Na 6.18

Theory ($C_{12}H_{10}O_2NH$) % $C_{12}H_{10}$ 71.05; %N 4.98; %Na 6.46

Molecular weight was determined cryoscopically from benzene.

Found M.W. 215.2

$C_{12}H_{10}O_2NH$ (calc.) M.W. 217.0

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Diphenylborinic Acid (IV)

Two grams of diphenyldioxyboronammonium are placed in a flask fitted with agitator. Twenty ml of water and twenty ml of isopentane are then poured into the flask. The contents are rapidly agitated and 1.5 ml concentrated hydrochloric acid, diluted in 15 ml of water are then added to the reaction flask. After half hour agitation the isopentane layer is separated and cooled to -70°C . The colorless isopentane supernatant is decanted from the solids. 1.5 grams of solid substance were obtained.

The reaction product was dried under vacuum at room temperature until constant weight was obtained (0.002 - 0.003 grams for 5 min.) Melting point of dried material was found to be -35 - -33°C .

Found % C_6H_5 78.18 %B 5.39

Theory ($\text{C}_{12}\text{H}_{12}\text{B}_2\text{O}_2$) % C_6H_5 77.08 %B 5.40

Diphenylboric Acid Anhydride (V).

Two grams of diphenyldioxyboronammonium are shaken for 15 minutes with 15 ml of water acidified with 1.5 ml of concentrated hydrochloric acid. Reaction products are extracted with ether which is then evaporated off under vacuum. The residue is further heated for 5 minutes at 70 - 80°C . Upon cooling the residue solidifies into a solid crystalline mass. The solid residue is then filtered (sharried) in 10 ml of isopentane, sucked dry, and then washed with more isopentane and dried under vacuum. 1.46 gms of product are obtained with m.p. 131°C . After recrystallization from benzene or from a mixture of benzene and isopentane, the product obtained had a m.p. 131 - 132°C . Diphenylboric acid anhydride, obtained by Na_2O , melted at 116 - 118°C .

Found %C 83.12; H 6.05; C_6H_5 89.42; B 6.21

Theory ($\text{C}_{24}\text{H}_{20}\text{B}_2\text{O}_2$) % C 83.54; H 5.84; C_6H_5 89.99; B 6.20

Molecular weight was determined cryoscopically from benzene.

Found M.W. 343.9

Calc ($\text{C}_{24}\text{H}_{20}\text{B}_2\text{O}_2$) M.W. 345

The yield of diphenylboric acid anhydride represents 92.8% theory. Diphenylboric anhydride is a colorless, crystalline material, quite soluble in methyl and ethyl alcohols, slightly soluble in cold benzene, soluble in hot benzene and insoluble in isopentane.

Diphenyldioxyboronpotassium:

1.1314 grams (0.00328 moles) of diphenylboric acid anhydride are dissolved in 7.62 ml of 1N potassium hydroxide. The resulting solution is evaporated

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in a vacuum dessicator. Solid residue is recrystallized from benzene - alcohol (20:1) mixture, sucked dry, washed with benzene and vacuum dried. Yield - 1 gram of material with m.p. 66-67°C. The substance is soluble in water and alcohols, and insoluble in isopentane, benzene and chloroform.

To determine percentage of potassium content, a known weight of the above obtained product is heated for half an hour with 1N sulfuric acid; the excess acid is then titrated with 1N sodium hydroxide.

Found % C_6H_5 64.66; B 4.16; K 16.55

Theory ($C_{22}H_{12}BO_2K$) % C_6H_5 64.78; B 4.54; K 16.42

Literature References

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